

COAL WEATHERING: CAUSES, EFFECTS AND IMPLICATIONS

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INTRODUCTION

If it is meaningful to single out one characteristic of coal as having unique importance, that designation would have to go to the dynamic nature of coal's chemical and physical properties. The chemical and physical properties of coal can and often do undergo substantial changes after removal of the coal from its natural environment. This phenomenon is known as weathering and can alter the coal's calorific value, beneficiation, coking, liquefaction, and gasification characteristics. Weathering also influences standard tests and other experimental results, and thus has important implications with respect to fundamental research on the structure and properties of coal. This short review focuses on the incomplete state of our knowledge of the causes, effects and implications of coal weathering.

CAUSES AND EFFECTS OF COAL WEATHERING

Weathering commences once the coal is unearthed and/or removed from the coal seam unless precautions are taken to prevent its exposure to oxygen (air) and changes in temperature and humidity. The exposure of coal to and its subsequent reaction with the oxygen in air is recognized as the most important contributor to weathering. The reaction of the coal with oxygen occurs readily at ambient temperature, results primarily in oxidation of the coal's organic constituents, and leads to an increase in the oxygen content and a decrease in the atomic hydrogen-to-carbon ratio of the coal (1-5).

The general outlines of the oxidation of coal's organic constituents by oxygen have been well characterized. Peroxides have been detected as transient intermediates in the early stages of coal oxidation (3,6,7), and it is generally thought that decomposition of the peroxides leads to creation of the new oxygen-containing functional groups (3,6-13). The formation of hydroxyl, carbonyl and carboxyl groups, and ether linkages have been detected or inferred from wet chemical and spectroscopic data (4,7,12-21). In general, the chemical structural changes that accompany coal's oxidation at low temperatures (from ambient to 200°C) by molecular oxygen are strongly dependent upon coal rank, particle size, oxygen partial pressure, moisture content, and temperature (1-5,17,22,23). Considerable uncertainty still exists, however, concerning the mechanisms whereby the peroxides are formed and subsequently decompose.

Perhaps the most elusive aspect of the reaction of coal with oxygen has been identification of the initiation reaction, the step by which the oxidation reaction gets started. Although the oxygen molecule has two unpaired electrons, one on each oxygen atom, and behaves as a diradical ($\cdot O-O\cdot$) it is too unreactive to be the species which actually oxidizes the coal. However, the fact that coal already contains substantial concentrations of carbon radicals (12,24-26) suggests the possibility that initiation may occur by reaction between molecular oxygen and a carbon radical in the coal to form a peroxy radical (Coal-OO \cdot). The peroxy radical could then serve as the initiator for free radical chain reactions which lead to peroxides and their decomposition products. The evidence for free-radical chain processes for the decomposition of the peroxides, however, is not unequivocal. Since water, a protic solvent, is invariably present in coal and has been observed to facilitate the oxidation of coal by oxygen (2,3,5,22,23) the decomposition of the intermediate peroxides might also occur, at least in part, via ionic reaction mechanisms (27). Clearly, many of the mechanistic aspects of the oxidation of coal by oxygen remain unresolved and present challenging problems for further exploration.

The reaction of coal with oxygen is also notorious for its idiosyncrasies. One of these is that the thermoplastic properties of bituminous and subbituminous coals are often extensively altered long before changes can be detected in the coal's chemical composition (1,2,5,28,29). In general, exposure of the coal to oxygen at ambient temperature can result in a very rapid reduction in the fluidity that it exhibits when heated and a significant narrowing of its plastic temperature range (5,10,28-30). The loss of the coal's thermoplastic properties suggests that a more highly cross-linked macromolecular structure has been formed which will not easily melt and flow when heated. However, the exact nature of the changes that occur in the coal's macromolecular structure which adversely affect its thermoplastic properties remain points of considerable uncertainty and interest.

The weathering of coal's inorganic constituents, in sharp contrast to the situation with coal's organic constituents, is quite well understood. Except for the iron bearing mineral pyrite which is readily air-oxidized, the coal's inorganic constituents apparently remain unchanged by weathering (31-33). The pyrite in coal is oxidized initially to iron sulfates, which are then transformed to iron oxyhydroxide (33). Pyrite oxidation, as expected, is accelerated by increasing humidity, temperature, and oxygen partial pressure. Although oxidation of the coal's organic and inorganic constituents occur simultaneously, they are generally regarded as quite separate processes.

Another contributor to weathering is the stresses caused by cyclic sorption and desorption of moisture which produce fissures and cracks that mechanically weaken the coal (2,5,34). This decrepitation phenomenon is referred to as slackening. The thermal cycling of coal also contributes to slackening. Slackening is much more rapid and extensive for lignites and subbituminous coals than for higher rank coals (5,34). Slackening can also accelerate oxidation by increasing the exposed surface area of the coal to air. Although oxidation can be accelerated by slackening, its possible participation in and importance to slackening has not been stressed or studied. The oxidation of coal's organic constituents could participate in slackening through the creation of new hydrophilic sites which would promote moisture sorption.

TECHNOLOGICAL ASPECTS OF COAL WEATHERING

The changes in coal's chemical and physical properties produced by weathering may affect the suitability of the coal for existing and future technological uses. Coal's major domestic uses include: direct combustion for electricity generation and for industrial process heat, steam and power generation; and conversion to coke for steel production (35). Coal-based synthetic fuel (gas and liquid) and chemical technologies are currently under development. Coal-water and coal-oil slurries are also being investigated as potentially economical means of converting solid coal into a form suitable for transport through pipelines and use as a liquid-like fuel.

Oxidation reduces the calorific value of coal. Low rank coals will lose about 190 Btu-per-pound for each 1% increase in oxygen content while high rank coals will lose about 240 Btu-per-pound for each 1% increase in oxygen content (34). The oxygen content of freshly mined and crushed lignite coals can increase several percent in a matter of weeks when the coal is stored in air at ambient temperature. Such rapid oxidation can lead to spontaneous combustion of the coal under certain storage conditions (34,36).

Oxidation also converts coal to a more hydrophilic material which makes beneficiation more difficult. The purpose of beneficiation is to upgrade the quality of the coal so that it can meet specific end-use requirements. Beneficiation is primarily carried out to reduce the mineral matter (including pyrite) and clay content of the coal. Oxidation reduces the hydrophobicity-hydrophilicity differences between coal's organic constituents and mineral matter which, in turn, makes it more difficult to selectively separate mineral matter particles on the basis of their hydrophilic surface properties (37-39). This results in a reduction in the efficiency of beneficiation by flotation, agglomeration and flocculation processes.

The new oxygen-containing functional groups that are created when the coal is oxidized also increase its adsorptive affinity for polar molecules such as water as well as its water solubility (40-42). Hence, the dewatering and drying of coal becomes more energy intensive and less efficient as the coal's degree of oxidation increases. The stability and viscosity of coal-water and coal-oil slurries would also be affected by the more polar surface properties of particles of oxidized coal. Additionally, the peroxides produced during coal oxidation could potentially have a detrimental affect on the stability and viscosity of coal-oil slurries.

The detrimental effects of oxidation on a coal's suitability for producing high-quality metallurgical coke have been extensively studied (1,2,5,16,28,43) and are well understood from a practical viewpoint. The adverse effects include reduction in coke strength, coal bulk-density-control problems, overheated charges, carbon deposits leading to oven damage, coke handling problems, and reduced coke yields as a result of increased coke breeze, increased coke reactivity and decreased coking rate (1,2,5,16,43). One important effect of oxidation is to destroy the coal's thermoplastic properties which, in turn, prevents its organic components from adequately fusing and binding together during the coking process. This results in a reduction in coke strength and yield.

The effects of oxidation on coal's behavior during thermal processing can be predicted to be profound but have not been extensively investigated. The new oxygen-containing functional groups that are created when the coal is oxidized will lead to increased yields of carbon monoxide and carbon dioxide at the expense of tar and/or liquid yields during gasification, liquefaction, pyrolysis, and thermal depolymerization in non-hydrogen-donating solvents (1,2,4,43-47). The increased cross-linking of coal's macromolecular structure that accompanies oxidation will also reduce its swelling during heating, extractability by organic solvents, and tend to increase the molecular weight distribution of the extractable material and low-temperature pyrolysis tars (1,2,46,47). An enhancement of char surface area (by a factor of up to 10) and gasification reactivity (by a factor of up to 40) has also been observed as a consequence of the preoxidation of bituminous coals (48).

CONCLUSIONS

The changes brought about by weathering that affect the suitability of coal for existing and future technological uses have a very definite molecular basis. At a molecular level, however, we are for the most part at a very primitive level of understanding of the weathering process. In spite of the recent research interest that has been shown in this important phenomenon, insufficient definitive experimental data exist to permit a detailed mechanistic description to be written which accounts for this phenomenon's complexities and idiosyncrasies. The complexity of the coal itself contributes significantly to the experimental difficulties. Hence, progress in elucidating the mechanistic details of weathering will require a more aggressive approach and help from many disciplines.

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SELECTION AND CHARACTERIZATION OF LOW-RANK COAL SAMPLES

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INTRODUCTION

The collection of low-rank coal samples at the University of North Dakota Energy Research Center (UNDERC) includes coals from the major lignite and sub-bituminous coal regions of the United States. Primarily, the coals were collected to provide fresh, homogeneous, and well characterized samples for projects in coal science research at UNDERC. In the past, research has been performed on coal in which no information was reported or available on how the samples were prepared and stored, or on the geography and geology of the coal seam. Richard Neavel (1) pointed out that work on "poorly selected, poorly collected, poorly prepared, poorly preserved and poorly characterized coal samples will only lead us into further confusion." It is important that coal science research be performed with carefully collected, prepared, and documented samples so that the resulting data on coal properties, composition, and reactivity will be meaningful to other researchers.

In the past several years a great deal of interest has surfaced dealing with sample banks. The American Physical Society (2) identified the need for a sample bank of well-selected, characterized and preserved coal samples the lack of which has been a major obstruction in the past to advancement of coal research. A Coal Sample Bank Workshop was held in March 1981 sponsored by the Gas Research Institute and the U.S. Department of Energy to identify the need and problems associated with setting up a National Coal Sample Bank (3). It is our hope that the information presented in this paper will be of use to researchers interested in establishing a sample bank or interested in incorporating low-rank coal samples in existing sample banks. The motivation for such work at UNDERC is the need for this type of research to be accomplished for low-rank coals.

Channel samples of low-rank coals have been collected from various mines in North Dakota, Montana, Colorado, New Mexico, and Texas. The samples were carefully collected, homogenized, and stored in an inert atmosphere. The coals were prepared in several different sizes from -1/2 inch to -60 mesh and quantities from 15 kilograms to 250 grams. At UNDERC the coals will be used to study various coal features such as the distribution of inorganics, organic structure, ash and slag chemistry, physical and mechanical properties, and pyrolysis and extraction behavior. In addition, trace element analysis, proximate, ultimate, heat content, ash fusion, and ash analysis will be performed.

SAMPLE SELECTION AND COLLECTION PROCEDURES

The selection of coals was based either on some desired unique characteristics such as sodium content, or slag viscosity, or on production tonnage. The goal is eventually to have a set of coals available which represent a wide range of coal properties characteristic of low-rank coals. The selection and preparation of coals will be an ongoing project at UNDERC for at least two more years and the total suite of samples will extend beyond the coals collected to date. The coal ranks to be included range from low-grade lignite to high-rank subbituminous.

When a mine has been chosen for sampling, a pit within the surface mine is selected, based either on some unique characteristic or on ready accessibility to the pit. A "typical section" is selected for sampling which is free of faults, slumping, or evidence of groundwater flow. The face of the seam or seams to be sampled is cleaned to expose fresh nonweathered coal free from extraneous mineral matter which may have fallen from the overburden. The coal seam is measured and a megascopic description is made of the coal and associated sediments. A channel sample is collected to provide approximately 100 kilograms of coal. In some cases, one-kilogram samples are also collected at various intervals throughout the seam, including overburden, interburden (if two seams are sampled) and underclay, to study the within-seam variability. All samples are sealed in plastic bags and transported to UNDERC for preparation. A list of samples collected through November 1983 is in Table 1.

TABLE 1
LOW-RANK COALS COLLECTED

<u>Mine</u>	<u>Rank</u>	<u>State</u>	<u>Region</u>
Abasloka (Sarpy Creek)	Subbituminous	Montana	Powder River
Indian Head	Lignite	North Dakota	Fort Union
Beulah (High-Na)	Lignite	North Dakota	Fort Union
Beulah (Low-Na)	Lignite	North Dakota	Fort Union
Gascoyne (Red Pit)	Lignite	North Dakota	Fort Union
Gascoyne (Blue Pit)	Lignite	North Dakota	Fort Union
Velva	Lignite	North Dakota	Fort Union
Spring Creek	Subbituminous	Montana	Powder River
Falkirk	Lignite	North Dakota	Fort Union
Glenharold	Lignite	North Dakota	Fort Union
Colorado Coal Co.	Subbituminous	Colorado	Green River
Navajo	Subbituminous	New Mexico	San Juan
San Miguel	Lignite	Texas	Gulf Coast
Martin Lake	Lignite	Texas	Gulf Coast
Savage	Lignite	Montana	Fort Union
Center	Lignite	North Dakota	Fort Union

The channel sample is crushed, split, and stored in plastic or glass containers under an argon atmosphere. The crushing is done using a hammer mill. A diagram which illustrates the procedure used for preparing the coals is shown in Figure 1. The final splitting of the -60 mesh coal is done by a rotary riffle in an argon-purged glove box. These samples are stored in plastic or glass containers which are in turn sealed in a plastic pouch. The -8 mesh coals are stored in plastic containers and purged with argon.

The samples collected at various locations within the seam are prepared for selected characterization techniques, such as petrography of separated lithotypes; x-ray diffraction of the overburden; interburden; underclay; and trace element analysis. This type of work is being done to examine the variability of organic and inorganic constituents within the seam and to understand interrelationships between coal properties.

RESULTS AND DISCUSSION

The geologic and geographic description of the sampling area along with the analytical determinations will be available for all samples. The types of analytical results being obtained include proximate, ultimate, heat content, ash fusion, ash analysis, and trace element analysis. As an example, the results obtained for Indian Head lignite will be summarized here. Table 2 summarizes the geographic and geologic description of the Indian Head Mine. The results of the analytical determinations for the traditional ultimate, proximate, heat content and ash analysis are summarized in Table 3. The trace element determinations performed by neutron activation analysis (NAA) are listed in Table 4. The NAA analyses were made by North Carolina State University (4).

TABLE 2
GEOGRAPHIC AND GEOLOGIC DESCRIPTION
OF INDIAN HEAD MINE

County	Mercer
State	North Dakota
Town	Zap
Basin	Williston
Group	Fort Union
Formation	Sentinel Butte
Bed	Beulah-Zap
Age	Paleocene
Grand Forks Number	83-0008
Sampling Date	11/83

The information shown in Tables 2-4 is steadily supplemented by characterization data from several research groups within the UNDERC Coal Science Division, which include Ash and Slag Chemistry, Organic Chemistry, Distribution of Inorganics and Geochemistry, Physical Properties and Moisture, and Coal Reactivity. Samples of lithotypes have been separated for characterization by many of the above techniques to supplement the "whole coal" data. Petrography is also being performed on the homogenized channel sample and the separated lithotypes.

SUMMARY AND CONCLUSIONS

The low-rank coals have been collected to obtain coals which represent a broad range of low-rank coal characteristics. These coals are carefully collected, prepared, and stored under an argon atmosphere. These samples are not comparable to those in a premium sample bank, because they are stored at room temperature and are not collected in large reserve quantities. All the data generated will be entered in a computer system and can be readily accessed. The results of studies on these coals will provide insight into the interrelationships of various coal properties, both with each other and with coal-specific process responses.

TABLE 3
RESULTS OF ANALYSES FOR INDIAN HEAD LIGNITE

<u>Ultimate Analysis</u>	<u>Wt % (as received)</u>
C	44.08
H	6.36
N	0.64
S	0.38
<u>Proximate</u>	
Moisture	34.0
Volatile Matter	27.4
Fixed Carbon	33.8
Ash	4.8
<u>Heat Content</u>	7329 Btu/lb
<u>Ash Analysis</u>	<u>Wt % of ash</u>
SiO ₂	21.1
Al ₂ O ₃	11.9
Fe ₂ O ₃	8.5
TiO ₂	1.0
P ₂ O ₅	0.5
CaO	20.9
MgO	6.5
Na ₂ O	11.9
K ₂ O	0.1
SO ₃	15.6
TOTAL	98.1

Mineralogy of coal by x-ray diffraction of low-temperature ash -
quartz
kaolinite
pyrite

Carboxylic acid group content 2.48 meq/gram.

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TABLE 4

NEUTRON ACTIVATION ANALYSIS OF INDIAN HEAD LIGNITE FROM NORTH DAKOTA

Element	Concentration, ppm
Titanium	110 \pm 20%
Iodine	<3.0
Manganese	4.6 \pm 5%
Magnesium	410 \pm 15%
Copper	<25.0
Vanadium	3.00 \pm 2%
Chlorine	16 \pm 20%
Aluminum	3020 \pm 1%
Samarium	0.4 \pm 2%
Uranium	0.3 \pm 10%
Lanthanum	4.7 \pm 1%
Cadmium	<1.0
Gold	<0.001
Arsenic	5 \pm 1%
Antimony	0.2 \pm 1%
Bromine	1.1 \pm 1%
Sodium	6220 \pm 1%
Potassium	<500.0
Cerium	7.80 \pm 10%
Calcium	3760 \pm 10%
Selenium	0.50 \pm 10%
Thorium	1 \pm 1%
Chromium	2 \pm 15%
Europium	0.09 \pm 10%
Ytterbium	0.4 \pm 20%
Barium	520 \pm 5%
Cesium	0.1 \pm 10%
Silver	<0.08
Nickel	<25.0
Scandium	1.3 \pm 1%
Rubidium	<5.0
Iron	3570 \pm 3%
Zinc	6.4 \pm 20%
Cobalt	1.60 \pm 1%
Silicon	<35,000.0
Molybdenum	<10.0

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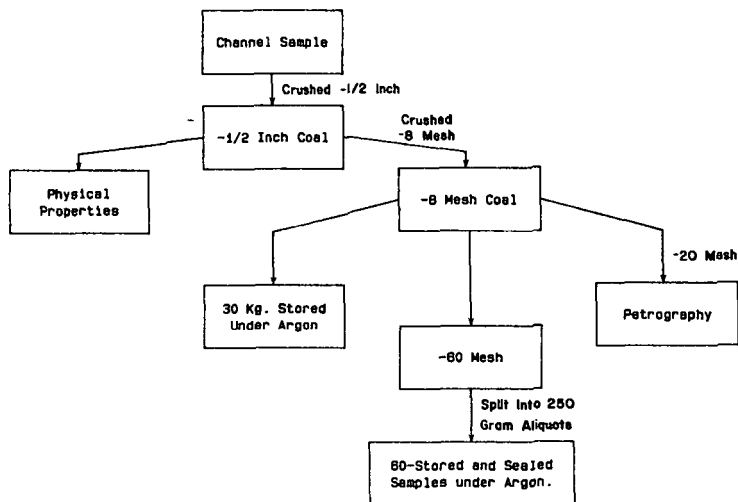


FIGURE 1. Schematic of sample preparation procedure for channel sample.

PROCESS FOR PRODUCING LOW-ASH, LOW-SULFUR COAL

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Introduction

Previous work has shown that ash-forming mineral matter, including iron pyrites, can be removed from coal by leaching fine-size coal with a hot caustic solution under pressure followed by washing with a dilute mineral acid (1-4). Recently, similar results have been achieved by leaching fine-size coal with hot sodium carbonate solutions. In both cases much of the mineral matter reacts with alkali to form acid-soluble compounds. Since sodium carbonate is readily available, low in cost, and much less corrosive than sodium hydroxide, it could be used advantageously. Unfortunately, iron pyrites are not leached as readily by sodium carbonate solutions as by caustic solutions. However, this difficulty can be circumvented by employing a multistep process in which the coal is first leached under oxydesulfurization conditions at 120-150°C to extract pyritic sulfur and then leached at higher temperature in the same alkaline solution but under non-oxidizing conditions to convert other minerals to acid-soluble materials. Pyrites readily react with oxygen dissolved in hot alkaline solutions to form water-soluble sulfur species (5,6). But if oxydesulfurization is conducted at the higher temperatures (250°C and above) required for the reaction of other minerals with alkali, coal losses will be excessive because of oxidation. Therefore a two-step leaching process is needed. The results of applying such a process to several bituminous coals are presented below.

Experimental Methods

Bituminous coals from several sources were used for the leaching experiments (Table 1). These coals were first ground to pass either a 200 or 400 mesh screen (U.S. standard). For some leaching experiments the coals were precleaned by a physical separation process which reduced both the ash and total sulfur contents. Precleaning involved mixing the ground coal with perchloroethylene and water, allowing the suspension to settle, and separating the two liquid layers as prescribed by Vivian (7). The coal macerals tended to concentrate in the

Table 1. Bituminous coals used in leaching experiments

Coal Seam	Location	Coal Form	Size, mesh	Ash ^a , wt. %	Tot. S ^b , wt. %
Illinois No. 6	Trivoli, IL	Raw	-200	12.75	3.71
Illinois No. 6	Trivoli, IL	Precleaned	-200	4.92	2.83
Pittsburgh No. 8	Moundsville, PA	Raw	-400	37.11	6.55
Pittsburgh No. 8	Moundsville, PA	Precleaned	-400	6.20	3.67
Lower Kittanning	Armstrong Co., PA	Raw	-200	17.87	10.61

^aDry basis

^bDry, ash-free basis

perchloroethylene layer whereas the minerals tended to concentrate in the water layer. This procedure was repeated five times with each coal which was precleaned. Approximately 87% of the Illinois No. 6 coal and 78% of the Pittsburgh No. 8 coal were recovered during precleaning. These values are expressed on an ash-free basis.

For most leaching experiments, 15g. of coal and 120 ml. of a 1.0 M sodium carbonate solution were placed in a 300-ml. stirred reactor made of type 316 stainless steel. The first leaching step involved reaction with oxygen dissolved in the solution under a partial pressure of 13.6 atm. at 150°C for 1 hr. (5, 8). During this step gas was bled from the reactor to avoid any build-up of gaseous reaction products in the system. Following the first step, the system was purged with nitrogen and the temperature of the system was raised to 250°C, whereupon the second leaching step was conducted for an additional 1 hr. under an inert atmosphere. After this treatment, the reactor was cooled quickly and the coal recovered by filtration. The filter cake was washed with water, dried for 4 hr. in an oven at 95°C, weighed, and sampled for chemical analysis. A portion of the leached coal was washed with a mineral acid (2M) by stirring the mixture in a flask for 30 min. After the acid treatment, the coal was recovered by filtration and the cake was washed with water, dried, weighed, and sampled for chemical analysis. These washing steps were conducted at either room temperature (25°C) or at the boiling point (100°C). In some cases, the regular washing step was extended by mixing the acid-treated coal with boiling water for 30 min., filtering, and then washing with more boiling water. Ash and total sulfur contents of the coal were determined by standard ASTM procedures (9).

Experimental Results

An initial set of experiments was conducted to see how effective the second leaching step was by itself when not preceded by the oxydesulfurization step. For this set of experiments raw coals were leached with a 1.0 M sodium carbonate solution at 250°C and then washed with 2M hydrochloric acid or sulfuric acid. When hydrochloric acid was employed, the acid washing step was always conducted at the boiling point and the final water washing step at room temperature. However, when sulfuric acid was used, the washing steps were conducted at various temperatures to see whether the temperature of the acid or the water had any effect.

The results of the first set of experiments presented in Table 2 indicate that the ash and total sulfur contents of the coals were reduced substantially by the treatment while the product recovery or yield was high. The results seemed to be affected by the source of the coal and the washing temperature, but it was not clear whether they were affected by the type of acid. The largest percentage reduction in either ash content or total sulfur content was achieved with Illinois No. 6 coal. In run 3 the ash content of Illinois No. 6 coal was reduced by 83% and the total sulfur content by 39%. The leached coal was washed with hot sulfuric acid in this run. Somewhat poorer results were realized when cold sulfuric acid was used. Also, extended washing with hot water had little effect when cold acid was employed.

The raw Pittsburgh No. 8 coal had a very high ash content which was reduced about one-third by the single-step leaching and washing treatment (Table 2). The total sulfur content was reduced 18-23% by this treatment. It seemed to make little difference which acid was applied to the leached coal.

The results achieved with Lower Kittanning coal were intermediate between those achieved with the other coals. Thus, the ash content was reduced 44-47% and the total sulfur content 25-27% when this coal was leached with an alkaline solution and washed with either of the hot acids. When the leached coal was

Table 2. Results of leaching raw coals with a hot alkaline solution followed by washing.

Run No.	Coal Seam	Acid Washing		Water Washing		Product %		
		Acid	Temp., °C	Type	Temp., °C	Yield ^a	Ash ^b	Tot. S ^a
1	Ill. 6	HCL	100	Regular	25	94	2.61	2.40
2	Ill. 6	H ₂ SO ₄	25	Regular	25	94	3.40	2.72
3	Ill. 6	H ₂ SO ₄	100	Regular	100	94	2.21	2.25
4	Ill. 6	H ₂ SO ₄	25	Extended	100	94	3.97	2.67
5	Pitts. 8	HCL	100	Regular	25	96	24.8	5.03
6	Pitts. 8	H ₂ SO ₄	25	Regular	25	96	24.5	5.34
7	Low Kit.	HCL	100	Regular	25	89	9.44	7.70
8	Low Kit.	H ₂ SO ₄	25	Regular	25	89	13.34	7.73
9	Low Kit.	H ₂ SO ₄	100	Regular	100	89	10.05	8.01

^aDry, ash-free basis

^bDry basis

washed with cold sulfuric acid, the ash content was reduced slightly less.

A second set of experiments was conducted in which the raw coals were leached first under oxydesulfurization conditions and then under nonoxidizing conditions at higher temperature (250°C). As the results shown in Table 3 indicate, this approach resulted in significantly greater sulfur removal. Under the best conditions, the total sulfur content of Illinois No. 6 coal was reduced 56%, Pittsburgh No. 8 coal 63%, and Lower Kittanning coal 86%. The total sulfur content seemed to be reduced by about the amount of inorganic sulfur present in the raw coal.

In most cases the two-step leaching method produced a lower ash content than the single-step leaching method. This result was probably due to the more complete removal of iron pyrites by the two-step approach. Also when two leaching steps were used, a cleaner product was obtained by washing with hydrochloric acid than by washing with sulfuric acid. However, when washing with hot sulfuric acid was followed by extended washing with hot water, the results approached those achieved by washing with hydrochloric acid. This effect can be seen in the case of Illinois No. 6 coal by comparing the results of run 14 with those of run 10 and in the case of Lower Kittanning coal by comparing the results of run 20 with those of run 16.

The coal recovery on a dry, ash-free basis was slightly lower for two leaching steps than for one leaching step. It seems likely that the lower recovery was due to coal oxidation in the first step. Although the coal loss was small, previous work (8) suggests that the loss could be reduced to an even lower level by decreasing the temperature in the first step.

In the final set of experiments, precleaned coals were leached by the one-step and two-step methods utilized before with the raw coals. The leached coals

Table 3. Results of two-step leaching of raw coals followed by washing.

Run No.	Coal Seam	Acid Washing		Water Washing		Product %		
		Acid	Temp., °C	Type	Temp., °C	Yield ^a	Ash ^b	Tot. S ^a
10	Ill. 6	HCL	100	Regular	25	91	1.82	1.63
11	Ill. 6	H ₂ SO ₄	25	Regular	25	91	4.07	1.81
12	Ill. 6	H ₂ SO ₄	100	Regular	100	91	2.97	1.84
13	Ill. 6	H ₂ SO ₄	25	Extended	100	91	3.31	1.65
14	Ill. 6	H ₂ SO ₄	100	Extended	100	91	2.43	1.62
15	Pitts. 8	HCL	100	Regular	25	92	17.3	2.41
16	Low Kit.	HCL	100	Regular	25	85	2.38	1.49
17	Low Kit.	H ₂ SO ₄	25	Regular	25	85	5.69	1.93
18	Low Kit.	H ₂ SO ₄	100	Regular	100	85	3.21	1.96
19	Low Kit.	H ₂ SO ₄	25	Extended	100	85	5.20	1.60
20	Low Kit.	H ₂ SO ₄	100	Extended	100	85	2.74	1.55

^a Dry, ash-free basis^b Dry basis

were washed with hot hydrochloric acid, followed by water washing at room temperature. By using precleaned coals, very low ash contents were achieved with either the one-step or two-step leaching methods. As Table 4 indicates, the ash content of Illinois No. 6 coal was reduced to less than 0.5% and that of Pittsburgh No. 8 coal to less than 0.9% by either method. Thus by using a combination of physical and chemical cleaning the ash content of Illinois No. 6 coal was reduced 96% and the ash content at Pittsburgh No. 8 coal 98%. The combination of physical and chemical cleaning was particularly effective in the case of Pittsburgh No. 8 coal, since even the two-step leaching process by itself reduced the ash content of this coal only by one-half.

Combined physical and chemical cleaning also achieved lower total sulfur contents than was achieved by either method alone (Table 4). Physical precleaning made more of a difference when it was followed by the one-step leaching process than by the two-step process. However, the lowest sulfur contents were achieved when the two-step leaching process was applied to precleaned coals. Application of this combination reduced the total sulfur content by more than 60% in the case of either Illinois No. 6 coal or Pittsburgh No. 8 coal.

Conclusions

A coal leaching process for removing ash-forming mineral matter has been demonstrated. This process involves leaching fine-size coal with a hot, dilute sodium carbonate solution followed by washing with a dilute mineral acid and water. While much of the mineral matter reacts with the alkali at 250°C to form acid-soluble compounds, iron pyrites are incompletely reacted by the hot alkali alone. This difficulty can be overcome by using a two-step leaching process in which oxygen is introduced under pressure in the first step to convert the pyritic sulfur to water-soluble species. The temperature of the first step should be limited to 150°C

Table 4. Effect of coal precleaning on results of leaching experiments.

Run No.	Coal Seam	Coal Form	Leaching Steps ^a	Washed Product, %		
				Yield ^b	Ash ^c	Tot. S ^b
21 1	Ill. 6	Precleaned	II only	95	0.49	1.81
	Ill. 6	Raw	II only	94	2.61	2.40
22 10	Ill. 6	Precleaned	I & II	92	0.41	1.35
	Ill. 6	Raw	I & II	91	1.82	1.63
23 5	Pitts. 8	Precleaned	II only	95	0.88	2.55
	Pitts. 8	Raw	II only	96	24.8	5.03
24 15	Pitts. 8	Precleaned	I & II	93	0.76	1.92
	Pitts. 8	Raw	I & II	92	17.3	2.41

^aStep I: 150°C, 13.6 atm. O₂ pressure.

Step II: 250°C, inert atmosphere

^bDry, ash-free basis

^cDry basis

to minimize coal oxidation. The leaching process can be combined advantageously with physical precleaning in produce coal with less than 1% ash and markedly reduced sulfur content.

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OXYDESULFURIZATION OF COAL. FURTHER STUDIES OF OXY-ALKALINOLYSIS

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Although it is clear that increasing amounts of coal will be burned each year for decades, no satisfactory technology for the chemical "deep cleaning" of coal has been developed. This situation arises from the fact that the forms of organic sulfur in coals are chemically reduced, and therefore, relatively unreactive under most desulfurization conditions. Early attempts to develop "oxy-desulfurization" processes failed to take into account that organic sulfur is no more susceptible to free radical oxidation than are carbon and hydrogen; and thus, even though pyritic sulfur is removed by these processes no selective removal of organic sulfur can be accomplished.

The use of more sulfur-selective electrophilic oxidants to chemically clean coal was introduced by the Jet Propulsion Laboratory's development of a chlorine based process (1-3). Unfortunately, this powerful oxidant also chlorinates coal, replacing some of the carbon-hydrogen bonds with carbon-chlorine bonds; and as many as 20 chlorines per 100 carbons are introduced (1, 3). Removal of this inadvertently introduced chlorine became a new problem which has proved very difficult to solve. JPL has attempted to dechlorinate the intermediate product using a variety of conditions including hydrogenation at temperatures up to 700°C (2).

In the meantime, TRW, Inc. had shown that substantial amounts of organic sulfur are apparently removed from coal by heating it with molten caustic (4-6). Since the replacement of oxidized sulfur functions as well as chlorine by hydroxide ions are common reactions in both aliphatic and aromatic chemistries, we reasoned that electrophilic oxidation followed by treatment with strong base would be superior to either treatment alone.

On this basis, we developed a two-step process for the desulfurization of coal in which the coal is first mildly oxidized and then heated with alkaline materials. In our first report (7), oxy-alkalinolysis was demonstrated to be more effective than either chlorination or alkali fusion. We now wish to present results using bromine as the first stage oxidant and add a few model studies which shed additional light on the chemistry underlying the processes.

EXPERIMENTAL

General

Western Kentucky No. 9 coal from the Ames Lab coal library, which had been prepared and stored under O₂-free conditions, was used. Bromination of the coal and the alkali fusion of the brominated samples were carried out under N₂ atmosphere. Before use, the coal was sized to pass through a 200 US mesh screen. Methylene

*Operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82.

chloride, potassium hydroxide pellets (85%), potassium iodide, sodium thiosulfate, potassium dichromate, and soluble starch, all certified ACS grade, were used as obtained from commercial sources. AR grade bromine was used in the bromination of coal. The analysis of the samples were carried out by the Ames Lab Analytical Services.

Bromination of Coal

A typical procedure for the bromination of coal samples is described below:

To a well stirred mixture of 70 ml of CH_2Cl_2 and 50 ml of water was added an accurately weighed (about 2.50 g) sample of coal. While stirring the mixture vigorously, 3 ml (58.6 mmol) of bromine was introduced in three equal portions. Stirring was effected by ultrasonic irradiation. After a total of 60 min., the mixture was filtered through a previously weighed fluoropore filter (3 m, Millipore). The coal residue was thoroughly washed 8-10 times using 20-25 ml of water each time. The brominated coal was then dried under vacuum in an oven at 110°C . After drying, the gain in weight of coal was recorded.

Estimation of Bromine

In a separate series of experiments, the bromine left unreacted after the bromination of coal was estimated by adding excess of KI to the filtrate and titrating the liberated I_2 with $\text{Na}_2\text{S}_2\text{O}_3$ previously standardized with $\text{K}_2\text{Cr}_2\text{O}_7$ using starch. This enabled us to determine the amount of Br_2 consumed by coal (0.5 g) during oxidation. The incorporated Br_2 was estimated from the elemental analyses.

Alkali Fusion

In a typical experiment 15-10 g KOH was at first fused at 380° in a steel reactor placed in a salt ($\text{NaNO}_3 + \text{NaNO}_2 + \text{KNO}_3$) bath and fitted with a N_2 inlet-outlet device, paddle stirrer and a port for loading coal. The molten mass of KOH was held at 380° until no more water was expelled. About 0.5 g of coal was then introduced and the molten mass was stirred at 380° - 390° for 30 min. After cooling, the contents of the reactor vessel were mixed with water and the resulting slurry was acidified with 1:1 HCl. The mixture was then kept over a steam bath for 30 min. and finally filtered through fluoropore (3 m, Millipore), washed very thoroughly with warm water, dried in an oven under vacuum at 110° overnight.

RESULTS

In order to understand the data, we will express changes in the coal on oxidation and KOH fusion in terms of atom ratios, most usually atoms per one hundred carbon atoms, $\text{xx}/100\text{C}$. This is equivalent to gram-atoms of X per 100 gram-atoms of carbon. This approach allows careful focus on changes in the organic fraction of the coal without regard to changes in the mineral matter.

The results of coal bromination are given in Tables 1 and 2 and a number of aspects of the reaction of bituminous coal with bromine are illustrated in Figure 1. Up to a ratio of more than 10 mmol of bromine per 100 g-atom of carbon, all of the bromine is consumed within the 60 minute reaction time. The weight of product increases markedly during the early stages of bromination, increasing by about one-third when 15 moles of bromine per 100 gram-atoms of carbon is

used. Increasing the ratio beyond 15 gives no further weight increase. As seen in Table 2, about one-fourth of the hydrogen in the coal is lost (see Figure 2a), even in the most lightly brominated samples, and sulfur falls off slowly and steadily with increased bromine consumption (See Figure 3a).

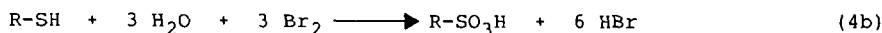
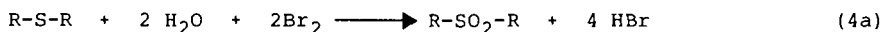
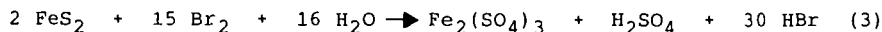
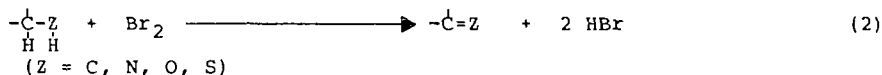
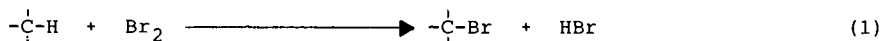
Table 3 shows the results of subjecting the preoxidized samples to fusion with KOH for 30 minutes at 380°C. Note that under these conditions, the sulfur level of the raw W. Kentucky #9 coal treated with KOH alone is reduced from 1.9S/100C to 0.7S/100C. There is a small increase in the sulfur level after fusion when insufficient bromine is used, but in general, the sulfur levels attainable in 30 minute KOH fusions for preoxidized samples decreases with increasing bromine consumption (See Figure 3b). Under the best condition a level of 0.1S/100C (94% desulfurization) is achieved. Bromine levels after fusion are uniformly low, confirming that organic halogen is removable by KOH fusion.

DISCUSSION

The Oxidation Step

Our previous paper established that chlorine is an effective oxidant (7); however, gaseous chlorine is not as easy to study in detail as is bromine because chlorine cannot be introduced as accurately nor kept in solution as easily. Therefore, we have determined the stoichiometry of the oxidation of coal with bromine, assuming that the result can be generalized to the other halogens.

Bromine is consumed in four phenomenologically identifiable processes: (1) substitution for hydrogen; (2) dehydrogenation of the coal; (3) oxidation of iron pyrite to sulfate and ferric iron; and (4) oxidation of divalent sulfur compounds to the tetravalent state, equations 1-4 respectively.



Given the following data: (1) the total bromine consumed, (2) the amount of bromine incorporated into the coal, and (3) the loss of hydrogen from the coal; one can calculate the amount of bromine consumed by processes 1 and 2, and then by difference, the amount of bromine consumed in oxidizing sulfur.

Table 4 shows that even at a bromine consumption level of 14 Br₂/100C, virtually all of the consumed bromine is accounted for without sulfur oxidation. The conclusion that some non-sulfur-oxidizing processes are very fast is also borne out by careful comparison of hydrogen loss versus sulfur reduction. Fifty-seven percent of the sulfur is removed under the most severe bromination conditions; roughly one-third of this sulfur is removed at a bromine-to-carbon ratio of 0.12. On the other hand, three-fourths of the

hydrogen consumed under the severest conditions has been removed at a ratio of 0.12.

Bromine in carbon tetrachloride or in water is used in most qualitative organic analysis schemes to diagnose the presence of (1) carbon-carbon unsaturation, (2) phenols, (3) compounds with relatively stable enol forms, (4) many amines, most notably anilines, and (5) other easily oxidized functional groups (8). Divalent organic sulfur compounds fall in this latter category along with hydroquinones and a few compounds possessing a very activated carbon-hydrogen bond. Thus, the concomitant consumption by coal of bromine in processes which do not oxidize sulfur is not surprising, and has been suggested before (9, 10); however, the extent to which it occurs is disconcerting.

The Alkali Fusion Step

The ratio of sulfur to carbon in the brominated coals drops modestly (from 1.5S/100C to 0.8S/100C) when the bromine to carbon ratio increases from 0.12 to 0.40 (See Figure 3a). However, over the same range, the susceptibility of the product to subsequent sulfur removal by KOH fusion is markedly enhanced. Fusion of the aforementioned samples with KOH leads to final sulfur values of 0.8S/100C and 0.1S/100C respectively (See Figure 3b). The organic sulfur in the sample treated with 40 Br₂/100C is clearly different from that in the sample treated with 12 Br₂/100C. On the basis of model compound studies reported previously (7), we are confident that it is the oxidation state of sulfur which has changed.

CONCLUSIONS

This study shows that preoxidation of coal samples by bromine markedly increases the efficiency of sulfur removal by molten caustic treatment. Under conditions which give a 65% sulfur reduction with KOH fusion alone, a preoxidized sample can be 94% desulfurized. That some hydrogen substitution and dehydrogenation processes are faster than sulfur oxidation has been demonstrated. The substitution reactions are probably phenol brominations and the replacement of active aliphatic hydrogen by bromine. The dehydrogenation reactions probably involve oxidation of easily oxidized carbon-carbon and carbon-oxygen bond systems.

**Table 1. Bromine consumed by
W. Ky. #9 Coal.***

$\left(\frac{\text{mol Br}_2}{\text{g-atom C}}\right) \times 100$ used	$\left(\frac{\text{mol Br}_2}{\text{g-atom C}}\right) \times 100$ cons'd
0	0
13.3	12.2
16.5	13.0
26.2	18.5
33.0	21.6
39.1	23.3

*One gram of W. Ky #9 coal contains .7086g (0.059g-atom) of carbon.

**Table 2. Product Analytical Data for
Brominated W. Ky. #9 Coal.**

Run No.	$\left(\frac{\text{mol Br}_2}{\text{g-atom C}}\right) \times 100$ used	$\left(\frac{\text{g-atom}}{\text{g-atom C}}\right) \times 100$		
		Br	H	S
1	0	0	86.0	1.9
2	11.9	7.1	68.3	1.5
3	15.9	8.3	68.5	1.2
4	23.8	8.6	65.6	1.1
5	31.8	9.4	62.2	0.8
6	39.7	9.8	61.9	0.9

**Table 3. Product Analytical Data
for KOH Fused Samples.**

Run No.	$\left(\frac{\text{g-atom}}{\text{g-atom C}}\right) \times 100$		
	S	Br	H
1	0.7	0.0	45.4
2	0.8	0.1	41.2
3	0.6	0.2	46.9
4	0.3	0.3	43.0
6	0.1	0.1	45.1

Table 4. Relative Stoichiometries of Bromine Consumption.

Run No.	$\left(\frac{\text{mol Br}_2}{100 \text{ g-atom C}}\right) \text{ consumed}$				
	Substitu- tion for H Process 1	Dehydro- genation Process 2	Sum of processes 1 and 2	Obs.	Obs.- (1+2)*
6	9.8	7.2	17.0	23.2	6.6
5	9.4	7.2	16.6	20.2	3.4
4	8.6	5.9	14.5	17.0	2.7
3	8.3	4.6	12.9	13.8	0.5
2	7.1	5.3	12.4	11.9	-0.5

*FeS₂ requires 3.4 Br₂/100 C; depending on functional group distribution, organic S requires 1.9-2.8 Br₂/100 C; total required for S oxidation is 5.3-6.2 Br₂/100 C.

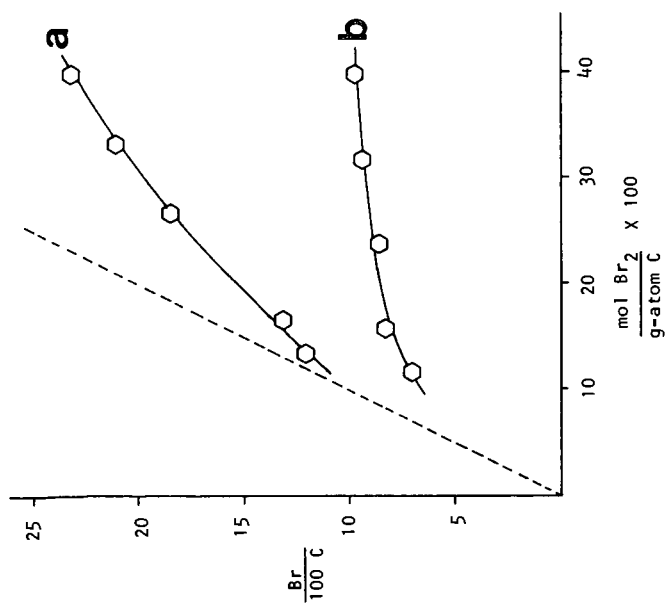


Figure 1. Reaction of Bromine with W. Ky. #9 Coal: (a) Consumption of Bromine and (b) Incorporation of Bromine as Functions of the Bromine to Coal Ratio (60 Minute Reaction).

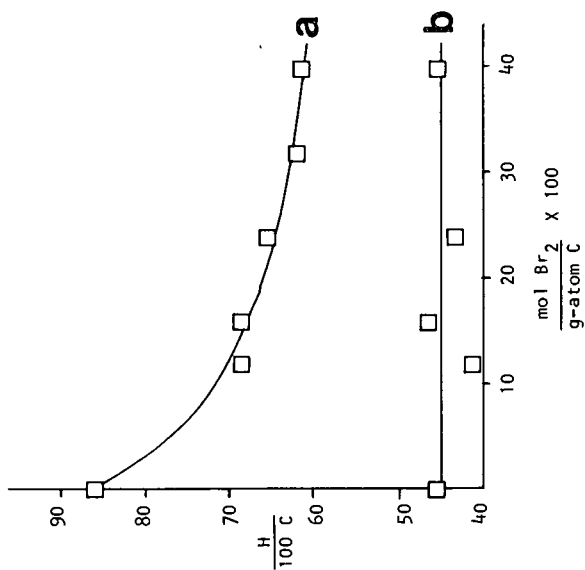
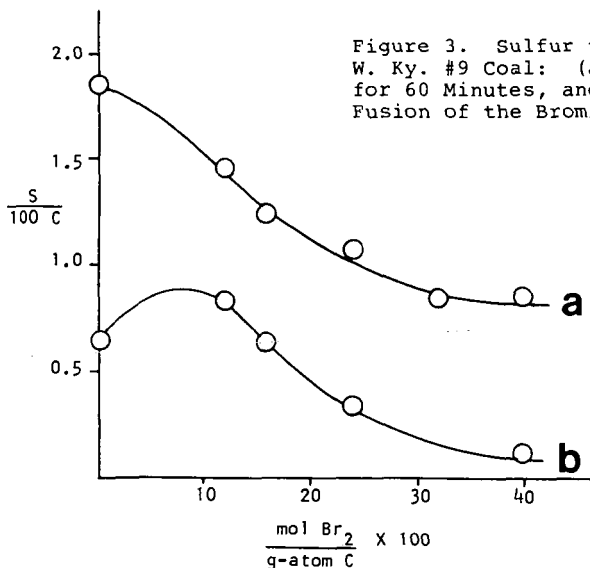


Figure 2. Hydrogen to Carbon Ratio in W. Ky. #9 Coal: (a) after Bromination for 60 Minutes, and (b) after KOH Fusion of the Brominated Samples.



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VOLATILITIES OF INORGANIC ELEMENTS IN COALS DURING ASHING

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INTRODUCTION

There are several reasons for requiring volatility information in coal:

a) Environmental

The flame temperature within the boiler furnace of a pulverized fuel power station may reach well above 1600°C when burning a bituminous coal. The higher the volatility of an element at temperatures of this magnitude then the higher will be the proportion of the element which will eventually escape to atmosphere, either in vapor form or in condensed form on unprecipitated fly ash particles. Elements which display some toxicity towards human, animal or plant life will therefore tend to impose a degree of detrimental impact on the environment.

b) Engineering design

The achievement of a satisfactory mass balance study of a coal combustion system must accommodate elements reporting to the primary bottom ash, precipitated and unprecipitated fly ash, and gaseous discharge components. Foreknowledge of volatility information can assist in the interpretation of data.

c) Analysis

Coal is a very complex heterogeneous matrix. Some techniques are suitable for the direct determination of many elements in whole coal samples while other techniques require an ashed sample.

d) Data base information

Many reports of elemental volatilities at various ranges of ashing temperatures and atmospheres have been published. An investigation covering a large number of elements, coal types, and ashing temperatures, would contribute significantly to an understanding of what could be expected under a given set of circumstances.

The literature on element volatility in coal is extensive. A summary has been compiled and discussed in the detailed NERDDP Report covering this work (1). When different reports are compared inconsistencies occur for many elements as ashing temperatures are raised from 370° to 2200°C. Several reports detailing ash derived from radiofrequency oxygen plasma ashing (RFA) at 150°C indicate quantitative retention of most elements studied making it a very suitable material for the analysis of inorganic elements in coal.

This investigation was designed to study the losses of 58 inorganic elements present at trace to minor concentrations in six coal samples.

EXPERIMENTAL

A set of six coals (four representative Australian bituminous coals and two US NBS standards, 1632A and 1635) were chosen to form the primary samples for this effort. Several other coals were selected to provide further information on specific elements.

Each of the coals was milled to less than 76 μm particle size in a slow speed Siebtechnik mill. The procedures for the preparation of the ash residues were as follows:

- 150°C(RFA) - multiple 0.6 g samples were processed in refractory boats with a layer loading of 1.5 mg/mm² in an LFE-504 Low Temperature Plasma Asher (150W power, 150 ml/min oxygen flow rate) until constant weight was achieved. The samples were removed from the asher three times daily and raked with a stainless steel spatula to present a fresh surface for oxidation. Total ashing time for each sample was approximately three days, except NBS1635 which required seven days.
- 370°C - samples were placed directly into a laboratory air oven maintained at the required temperature, and remained until constant weight was achieved (approx. 14 days).
- 815°C - samples were placed in a furnace at 200°C, and brought to 500°C over 30 min, transferred to a second muffle at 500°C and brought to 815°C over 30 min, then held at 815°C for 30 min.
- 1500°C - samples of 815°C ash were placed in a 10 ml platinum crucible (specially altered by the attachment of fine platinum wires to allow manipulation from above), lowered into the hot zone of a vertical tube furnace, and held at this temperature for 30 min. All of the residues from this procedure had fused, and were pulverized in a Siebtechnik mill.

The analytical methods employed for determining the 58 elements in this study were X-ray spectroscopy (XRF), instrumental neutron activation analysis (NAA), atomic absorption spectroscopy (AAS), inductively coupled plasma spectroscopy (ICP), specific ion electrode potentiometry (ISE), and optical emission spectroscopy (OES). The specific details for these procedures have been previously published (1-6). The elements determined by each technique are summarized in Table 1. In many cases, where possible, elements were determined by several methods.

RESULTS AND DISCUSSION

An element was considered volatile if the difference between its concentration in the starting coal and in the ash, on a normalized basis, was greater than the experimental uncertainty for a particular element. A greater than 20 percent change in concentration was usually required for the change to be considered significant. The volatility of an element was designated inconclusive when it was very near the experimental uncertainty or if different analytical techniques indicated conflicting results.

The results of this study are summarized in Table 2. Only six of the 58 elements investigated undergo some degree of volatilization at temperatures up to 815°C. This group of elements--boron, bromine, cadmium, fluorine, mercury, and selenium--was augmented at higher temperature, 1500°C, by a further ten--arsenic, gallium, germanium, manganese, potassium, sodium, strontium, thallium, yttrium, and zinc--which were each volatilized from at least one of the coals. Note in Table 2 that Bi, Gd, Ho, and Te were below the limits of detection for all the six coals

investigated, eliminating the evaluation of volatility trends. Other elements (In, Dy, and P) were below detection in four of the coals. Results for NBS1635 indicated seventeen elements were below limits of detection. Thus, under the oxidizing conditions prevalent during the preparation of the various coal ashes, there were 38 elements which at no stage were observed to undergo significant volatilization.

RFA Volatilization

Mercury was consistently retained in the RFA residue of each of the six coals studied in this project. Conversely, the literature has reported the consistent and unambiguous loss of mercury. Attention to details of RF ashing, which influence the actual temperature of the oxidation, possibly explains this discrepancy. For example, the sample layer loading within each sample container inside the RF ashing instrument, the particle size, the mineral matter content, and the chemical composition, could all play a part in influencing the localized temperature.

The implication of the literature was that bromine is volatilized. The 'difference' between the literature and the present work derives from there being a variable loss observed herein, with four coals showing definite volatilization, one (SC143B) showing retention, and one (NBS1635) being inconclusive.

Selenium is generally regarded as a relatively volatile trace element though consistently is retained under the conditions of RFA preparation. There was, however, the single incidence with SC146 in the present work for which this element was considered to have been volatilized.

Only fluorine was found to be volatilized significantly during the oxidation of each of the coals.

Low temperature ashing, although a time consuming procedure, is highly recommended for preparing coal samples for analyses where the analytical method to be used requires the carbonaceous material to be removed. Of all the elements surveyed in this study only a few (F, Br, B, and Se) indicated significant volatility. It is recommended that laboratories check their ashing procedures critically (especially for Hg) before attempting this approach however.

370°C Volatilization

At a temperature of 370°C selenium was significantly volatilized from four of the six coals. In contrast the literature implies that selenium is consistently lost under these ashing conditions.

Boron occupies a curious and special position, with regard to the volatility data in this work as well as to those literature reports which have addressed the lower temperature volatilization behavior of this element. Boron volatilization data implied that there were occasionally substantial losses at 370°C. However, the 815°C ash data for the above-mentioned coals indicated a retention of boron. The results of the present study may be interpreted in terms of respective kinetics for low temperature volatilization and higher temperature oxidative retention. Boron is well known to be predominantly associated with organic matter in coals, an affiliation which has been proposed to explain the high emissions of this otherwise refractory element in the stack gases from coal fired power stations (7). The competing reactions of organo-boron volatilization and oxidation must be considered to favor the former at low temperatures and the latter at higher temperatures. The absence of 370°C loss for all coals, plus the variable behavior with the NBS1635 ashes, implies a probable strong dependence of boron volatility upon the chemical forms of the element present in individual coals, and possibly localized oxidative conditions during the preparation of the ash residues.

815°C Volatilization

The 500°-900°C temperature range ashes have been the most extensively investigated in the literature, with 15 separate works being available for comparisons with the results of the present study. Fourteen elements listed as "inconclusive" retention from literature reports were found to be essentially retained in the 815°C ash in this study. This included Sb, As, B, Cr, Co, Cu, Ga, Pb, Mn, Mo, Sn, Ti, V and Zn. Cadmium was found to be volatilized in several coals at 815°C in contrast to literature reports where retention was claimed. All coals studied showed some significant loss of Se at this temperature. Sodium was found to be essentially retained in the six coals tested.

1500°C Volatilization

The very high temperature to which these ashes were heated yielded an increase in elemental volatilities from all coals. However, there was no element which was lost from every one of the six primary coals. Thallium was lost from five coals, arsenic from four, gallium and yttrium from two each, and germanium from one bituminous coal, with manganese, potassium, sodium, strontium, and zinc from NBS1635 only. In the literature, one report indicated consistent and complete volatilization of arsenic by 1400°C, while the alkalis, sodium and potassium, as well as strontium, were considered involatile. Cobalt and vanadium were not observed to have been volatilized from any of the coals of this study.

Environmental Considerations

The volatilities of the inorganic elements studied in this project are of considerable interest in relation to the classifications of potential environmental concern as assigned in a National Research Council Panel Report to trace elements in reference to impact on environmental quality and health (8). The exact reasoning behind one or other designation for a particular element is quite complex, taking into consideration such aspects as toxicity to human, animal and plant life, chemical reactivity following release into the environment, leachability by groundwaters, amongst others. These elements are categorized in Table 3 and listed also according to the following volatility designations as observed in this study:

high (volatilization generally observed in coals below 815°C)

moderate (volatilization observed for coals below 1500°C)

Low (volatilization negligible at 1500°C)

Table 3 indicates that B, Cd, Hg, Se, and F are classified as moderate or greatest environmental concern and also high volatility. Both B and F have relatively large concentrations in most coals (>50 ppm), Se is generally ~1 ppm or higher, and Hg and Cd tend to be lower than 1 ppm. This combination of toxicity, concentration, and volatility gives some qualitative emphasis to an elements possible environmental impact.

CONCLUSION

The investigation of the volatility behavior of 58 elements in coals, from analyses of the whole coals and their ashes prepared under static oxidizing conditions at temperatures up to 1500°C, showed that only very few elements are lost up to 815°C. This gives further support for utilization of low-temperature plasma ashing to prepare coal samples for analysis. By 1500°C, volatilization losses of nearly one-third of the inorganic elements studied became appreciable.

The most probable factors affecting the volatility of an element are the ambient chemical and physical states. Volatilization will depend upon the distribution of the element between various mineral phases or organically associated

species in the coal, and upon the prevailing temperature and oxidizing or reducing conditions during combustion. Observations of boron and mercury volatilities under various conditions support this conclusion. Time effects may also be important, as completion of ashing under RFA and 370°C conditions takes many days. The present study could not, nor did it seek to, achieve a thorough assessment of these factors.

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Table 1. Methods Utilized for the Analyses of Coal and Coal Ash.

	NAA	XRF	OES	ICP	AAS	ISE		NAA	XRF	OES	ICP	AAS
Ag	X				X		Lu	X	X			
Al			X	X			Mg			X	X	
As	X	X					Mn	X	X	X	X	
B			X	X			Mo	X	X			
Ba	X	X	X	X			Na	X		X	X	X
Be			X				Ni	X	X	X	X	
Bi		X					P			X	X	
Br	X	X					Pb		X			
Ca			X	X			Rb	X	X	X		
Cd					X		Sb	X	X			
Ce	X	X					Sc	X	X			
Co	X	X	X				Se	X	X			
Cr	X		X	X			Si			X	X	
Cs	X	X					Sm	X				
Cu		X	X	X			Sn		X			
Dy	X	X					Sr		X	X	X	
Eu	X						Ta	X	X			
F						X	Tb	X				
Fe			X	X			Te		X			
Ga	X	X					Th	X	X			
Gd		X					Ti		X	X	X	
Ge		X					Tl		X			X
Hf	X	X					W	X				
Hg					X		U	X	X			
Ho		X					V		X	X	X	
In	X	X					Y		X			
K	X		X	X	X		Yb	X	X			
La	X						Zn	X	X	X	X	
Li				X			Zr		X	X	X	

Table 2. Elements with significant volatilization observed initially at indicated temperatures.

Coal Number (Rank Classification)	RFA, ~150°C	370°C	815°C	1500°C
SC143B (Bituminous)	fluorine	boron mercury	cadmium selenium	arsenic gallium thallium yttrium
SC146 (Bituminous)	bromine fluorine selenium	boron mercury	cadmium	-
SC147 (Bituminous)	bromine fluorine	boron mercury	selenium	arsenic cadmium thallium
SC151 (Bituminous)	bromine fluorine	boron mercury selenium	-	arsenic cadmium germanium thallium
NBS1632a (Bituminous)	bromine fluorine	boron mercury selenium	-	arsenic cadmium gallium thallium yttrium
NBS1635 (Subbituminous)	boron fluorine	mercury selenium	-	manganese potassium sodium strontium thallium zinc

Note 1. The following elements may be volatilized at 1500°C in the indicated coals, however the data is either not sufficiently accurate for a firm conclusion to be drawn or there is unresolved conflict between data from different analysis techniques:

Ce (NBS1635) Pb (SC147)
Ga (SC146) K (NBS1632)

Note 2. Boron was lost only at 370°C from SC146, SC147, SC151 and NBS1632a, but from the RFA, 370°C and 1500°C residues from NBS1635. No B was lost from any 815°C ash preparation.

Note 3. Those elements which were below the limits of detection are summarized as follows:

All coals	Bi, Gd, Ho, Te	NBS1632A	Dy, In
SC143B	Dy, In, P	NBS1635	As, Br, Cd, Cs, Co, Dy
SC146	In		Ge, Hf, In, Lu, Rb, Sb,
SC147	In, P		Sb, Sn, Ta, Th, U, Yb

Table 3. Volatility classifications of 'elements of concern'

NRC PECH Panel Classification (8)	element	volatility
greatest concern	arsenic	moderate
	boron	high
	cadmium	high
	lead	low
	mercury	high
	molybdenum	low
	selenium	high
moderate concern	chromium	low
	copper	low
	fluorine	high
	nickel	low
	vanadium	low
	zinc	moderate
minor concern	antimony	low
	barium	low
	bromine	high
	chlorine	-
	cobalt	low
	germanium	moderate
	lithium	low
	manganese	moderate
	sodium	moderate
	strontium	moderate
radioactive	thorium	low
	uranium	low
elements of concern but with negligible concentrations	beryllium	low
	tellurium	-
	thallium	moderate
	tin	low

Refer to text for volatility classification bases.

DESCRIPTIVE OXIDATIVE PROFILES FOR PYRITE
IN THE LOW TEMPERATURE ASH COMPONENT OF COALS
BY DIFFERENTIAL THERMAL ANALYSIS

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INTRODUCTION

There are two forms of FeS_2 which may be present in coals. Pyrite is the cubic modification and marcasite is an orthorhombic form. Marcasite is referred to as the low temperature form. Of the two, pyrite is by far the most abundant in the mineral matter of coals. These sulfur-containing minerals are of special interest from an environmental standpoint since their combustion produces sulfur dioxide gas. The $\text{Fe}_2\text{O}_3(\text{s})$ product of oxidation contributes to the ash material of coals along with combined $\text{SO}_x(\text{g})$ with any existing $\text{CaO}(\text{s})$ in the ash. The amount of iron and its oxidation state influence the ash fusion temperature.

The mechanism of oxidation of pyrite and marcasite in air has been the subject of much study and speculation (1-13). The techniques of differential thermal analysis (DTA), thermogravimetry (TG), and derivative thermogravimetry (DTG) offer direct methods for studying the oxidative behavior of these minerals. Thermal analysis data on the oxidation of sulfides, in general, are somewhat inconsistent. It has already been pointed out by several workers (8,11,13), the factors which seem to be important in such thermal analysis studies are good air circulation in the analyzer, constant experimental conditions, and small sample sizes. Kopp and Kerr (11) have reported that the oxidative peak temperature is lowered with decreasing particle size.

In the course of a detailed thermal analysis study dealing with low temperature ash (LTA) components of several pyrite containing coals from southwestern Illinois and eastern Kentucky, it was observed that the thermal analysis peaks obtained by DTA, TG, and DTG were, in many cases, either altered or shifted when compared to those exhibited by the individual minerals themselves. In the following study, some sample handling techniques, synthetic mineral mixtures, and low temperature ash materials are investigated in an attempt to explain some of these phenomena as observed in dynamic air atmospheres.

EXPERIMENTAL

The pyrite ore used in this study was obtained from Dr. O. Katkins, Department of Geology, University of Pittsburgh at Johnstown (UPJ), Johnstown, PA. A second pyrite specimen was purchased from Wards Natural Science Establishment, Inc. (Rochester, NY). Both the UPJ and Wards specimen were subjected to careful mechanical grinding prior to use. The thermal curve shown for pyrite in Figure 1 of this paper is that of the UPJ specimen.

The high purity marcasite specimen (Iowa, USA) was obtained from F.I. Fiene, Institute for Mining and Mineral Resources (IMMR), University of Kentucky, Lexington, KY. All low temperature ash specimens of this study were also obtained from IMMR. All pyrite estimates given for the LTA specimens were made

using a Phillips Model 3100 X-Ray Diffractometer located at IMMR. The sulfur analysis values for these LTA specimens were obtained using a Perkin-Elmer Model 240C Elemental Analyzer with the Sulfur Analysis Kit. A Perkin-Elmer Model 240DS microcomputer data station was used with the elemental analyzer. These values represent all of the sulfur contained in the LTA specimen except for the small quantity which may be present as calcium sulfate or gypsum.

All DTA thermal curves reported in this work were obtained using a Perkin-Elmer microcomputer-based DTA 1700 High Temperature Differential Thermal Analysis System. Only the DTA mode of operation of this instrument was used in the studies presented here. Ceramic liners (60 mm³) were used in the DTA sample holder cup. However, it was found that platinum liners could also be used with small pyrite samples and with all LTA specimens of this study in dynamic air purge. In these cases, the pyrite oxidation is complete prior to the decomposition temperature for pyrite.

RESULTS AND DISCUSSION

Pyrite and Marcasite Specimens

In this study, both pyrite and marcasite specimens exhibited broad multi-step DTA oxidative profiles when DTA samples of approximately 21 milligrams were studied in an undiluted fashion. The temperature of initiation of the exothermic activity was ca. 360°C when the specimens were heated at 10°C per minute. The temperature range of the exothermic oxidative profile was found to be highly dependent upon sample size and heating rate. Smaller sample sizes and slower heating rates gave oxidative profiles which were more singular in nature for these undiluted samples.

Dilution of the pyrite or marcasite with alumina or inert material allows a better oxidant availability to the sample material and more closely simulates the distribution of pyrite in natural specimens such as the LTA component of coals. Figures 1 and 2 give the DTA oxidative thermal curves for diluted samples of pyrite and marcasite, respectively. As one can see, very similar oxidative profiles are obtained for these diluted specimens. The major difference which was observed in these studies is that the sharp exothermic peak maximum for the FeS₂/Al₂O₃ mixture was, on the average, 25°C lower in temperature for the marcasite specimens than the pyrite specimens of this study. No such difference was observed for the broad exothermic profiles associated with the larger undiluted samples.

Herrin 6 LTA Specimen

The oxidative profiles for the pyrite component of low temperature ash materials from coals are somewhat different from those given for pyrite and marcasite in Figures 1 and 2. The DTA thermal curve, shown in Figure 3, is that which was obtained for a LTA specimen of the Herrin 6 seam (southwestern Illinois). As one can see, a multi-step exothermic oxidative region with peak maxima at 407°C, 464°C, and 508°C is obtained. This LTA specimen was analyzed to contain 9.9% sulfur and the pyrite and marcasite content was estimated by XRD to be 19% and 2%, respectively. Since this coal was subjected to low temperature ashing in an oxygen plasma where temperatures near 100°C are reached, the presence of considerable iron sulfates is likely. This turns out to be the case as is described in a paper (17) which follows this writing. Rao and Gluskoter (14) found the iron sulfates content in 44 specimens of the Herrin 6 seam to vary from 0 to 32 percent. In general, however, the iron sulfate minerals rarely comprised more than 7 percent of the LTA matter for the Herrin 6 seam.

Pyrite/Iron Sulfate/ Al_2O_3 Synthetic Mixture

Since ferrous sulfate is known to be the intermediate step in the total oxidation of pyrite (4), a study was performed to determine the effect of the presence of iron (II) sulfates on the oxidative profile of pyrite. Figure 4 shows the resulting DTA, TG, and DTG oxidative thermal curves obtained from a synthetic mixture containing 23.1% pyrite, 13.76% $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, and 63.1% Al_2O_3 diluent were heated at 10°C per minute in dynamic air atmosphere. Although not labeled in the DTA thermal curve, the exothermic region gives peak maxima at 465°C and 520°C with a relative minimum separating these at 478°C . The endothermic event beginning near 600°C is the normal ferrous sulfate decomposition as observed in dynamic air atmosphere (16). When this DTA pattern is compared with that observed in Figure 1 for the pyrite/ Al_2O_3 mixture, one will note that the presence of iron sulfates lowers the temperature of the major peak maximum by 27°C and also converts the oxidative profile to a clearly defined two stage event. One will note that the peak maximum at 465°C is in common with that in the LTA material for the Herrin 6 seam which gives a maximum at 464°C . The TG and DTG thermal curves in Figure 4 show that the exothermic peak at 465°C is associated with a weight gain and the one at 520°C is associated with a weight loss event. It should be pointed out that the pyrite/iron sulfate synthetic mixture exhibits an iron sulfate decomposition above 600°C while the thermal curves for pyrite/ Al_2O_3 mixture did not.

Variation of the Pyrite Exothermic Response with Pyrite Level in LTA Specimens

A study was performed to see how the oxidative profile varied with the pyrite level in a series of LTA ash specimens. For this study, LTA specimens from the Herrin 6 seam (southwestern Illinois), Hazard 8 seam (eastern Kentucky), and two specimens of the Hazard seam from two different locations in eastern Kentucky. Table I gives the estimated pyrite levels for three of the four LTA specimens as obtained by XRD techniques. The total sulfur, as assigned by the Perkin-Elmer 240C Elemental Analyzer, is also given for the LTA specimens. As one can see, the pyrite level varies from as high as 19% in the Herrin 6 specimen to a low of 2% in the Hazard 7 LTA specimen.

Figure 5 shows the DTA oxidative thermal curves obtained for these LTA specimens in a dynamic air purge of 50 cc/min. The sample weights used were 23.1 mg for the Herrin 6, 35.0 mg in the Hazard 8, 29.5 mg in the Hazard 7, and 28.7 mg of the Hazard 7A LTA specimen. One will immediately note that the middle exothermic event ($T_{\text{max}} = 464^\circ\text{C}$) in the Herrin 6 specimen is in common with the other 3 specimens. This event is observed at 464°C in the Hazard 8 LTA specimen and at 459°C in the Hazard 7A specimen. One will recall that this peak was also observed at 465°C in the synthetic pyrite/ FeSO_4 mixture. The temperature of this peak maxima decreases as the amount of pyrite decreases and thus occurs at 438°C for the Hazard 7 specimen which was estimated to contain only 2% pyrite.

From these thermal curves one might predict that the exothermic oxidative profiles become multi-peaked and show activity at higher temperatures as the pyrite level increases. This is in agreement with our previous experiments given earlier in this work. The temperature of onset of oxidation is very similar in all four of the LTA specimens even though the mineral content of the Illinois coal is quite different from the three Kentucky coal LTA specimens. All four LTA specimens contained significant iron sulfate component. This iron sulfate level being less as the pyrite level decreases. This may be seen by the

decrease in magnitude and temperature of the decomposition peak observed at 667°C in the Herrin 6, 662°C in the Hazard 8, etc. This endothermic peak, in some cases, overlaps and predominates over less intense illite-smectite or smectite clay mineral dehydroxylation in these low temperature ash specimens.

The clay mineralogy was noticeably different in the four LTA specimens. For example, all three of the Kentucky coals contained detectable levels of kaolinite, as is evidenced by the exothermic ordering peak (spinel formation) at 968°C, 976°C, and 984°C in the Hazard 8, Hazard 7, and Hazard 7A, respectively. The Herrin 6 seam showed no evidence of kaolinite at the level of detectability of DTA. The double endothermic peak at 108°C and 150°C in the Herrin 6 specimen is due to the loss of interlayer water from both illite and illite-smectite mixed layer clay minerals. The lower temperature event (108°C) may also be due, in part, to the dehydration of iron sulfate species such as the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (melanterite), $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ (rozenite), and $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ (coquimbite). Likewise, the endothermic peaks in the Hazard 8 (113°C), Hazard 7 (111°C) and Hazard 7A (113°C) specimens are due to the same water loss phenomena. Because of the fact that the Hazard 7 specimen contains very little iron sulfate component, the thermal curves for the three Kentucky specimens indicate that these endothermic events are mostly due to the presence of illite and mixed layer clays containing illite clay mineral.

The Herrin 6 contained a measurable calcite component while the three Kentucky specimens did not. The endothermic peak at 890°C in the DTA thermal curve for the Herrin 6 seam is associated with the decomposition of calcite although it is sharpened by its association with the oxidation products of the pyrite. This will be discussed in detail in a paper which follows (17). One will also note that the clay mineral dehydroxylation endotherm (ca. 540°C) which is observed immediately after the pyrite oxidation is more distinguishable in the Hazard 7 and 7A specimens than in the Hazard 8 specimen. This is primarily due to the lower kaolinite and higher pyrite level in this specimen than is present in the two Hazard 7 specimens.

CONCLUSION

The temperature range as well as the nature of the exothermic oxidative profile for pyrite was found to be highly dependent upon sample size and heating rate. Smaller sample sizes and slower heating rates favor a more singular oxidative profile. Dilution of the pyrite or marcasite specimen with alumina or inert material allows a better oxidant availability to the sample material and more closely simulates the distribution of pyrite in natural specimens such as LTA specimens from coals.

The presence of iron sulfates lowers the peak temperature and converts the oxidative profile for pyrite specimens to a two stage event. Furthermore, pyrite specimens, as well as LTA specimens from coals, containing significant levels of iron sulfates were observed to exhibit a DTA endothermic event between 630°C and 670°C which is characteristic for the decomposition/oxidation of the iron sulfates component. This thermal event was absent from the DTA oxidative thermal curves for pyrite samples which initially contained no iron sulfates.

The DTA oxidative profiles for LTA specimens containing varying amounts of pyrite and iron sulfates showed that the exothermic oxidation of the pyrite component becomes more multistep in nature as the pyrite level increases. The iron sulfate content of the LTA material was observed to increase with the pyrite in the same specimen. This was reflected in the DTA thermal curves by the magnitude of the endothermic thermal event near 660°C. In the LTA specimens of this study, this iron sulfate decomposition/oxidation endotherm near 660°C in the DTA thermal

curve was observed to overlap and, in some cases, mask the less intense endothermic dehydroxylation peak of mixed layer clays which contain smectite clay mineral components.

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Table I

Pyrite and Total Sulfur Content
For The
Four LTA Specimens Of This Study

<u>LTA Specimen</u>	<u>Pyrite (XRD Estimate)</u>	<u>% Total Sulfur</u>
Herrin 6	19%	9.9
Hazard 7	2%	1.7
Hazard 7A	5%	3.8
Hazard 8	NA	6.5

NA = Not Analyzed

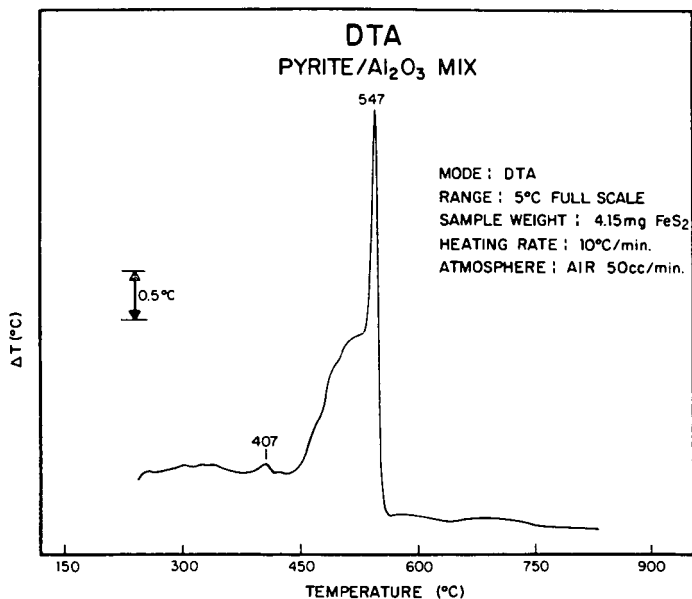


Figure 1. DTA Oxidative Thermal Curve for Pyrite/Al₂O₃ Mixture
Containing 4.15 mg of Pyrite

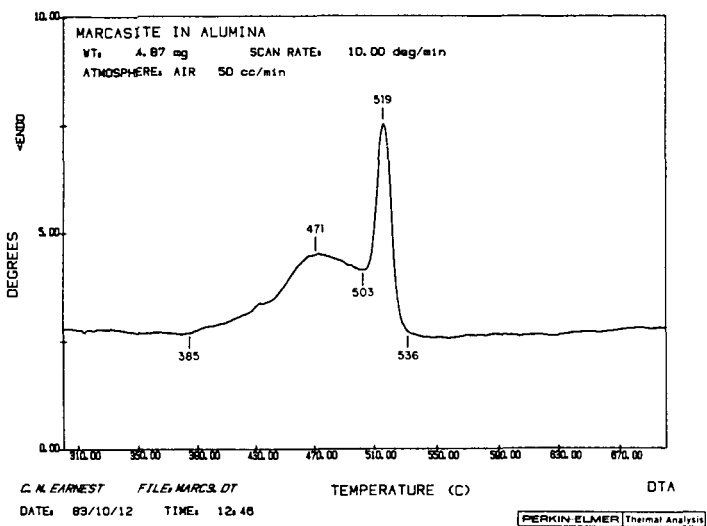


Figure 2. DTA Oxidative Thermal Curve for a Marcasite/ Al_2O_3 Mixture Containing 4.87 mg of Marcasite

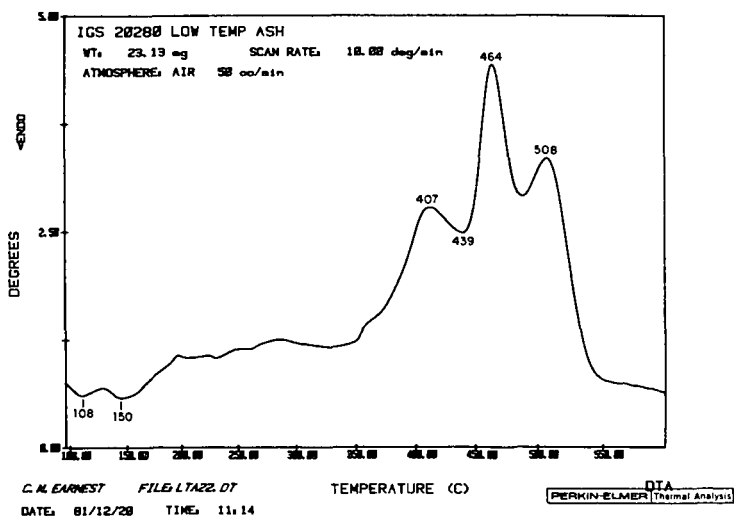


Figure 3. DTA Thermal Curve for Low Temperature Ash Component of the Herrin 6 Seam in Dynamic Air Atmosphere

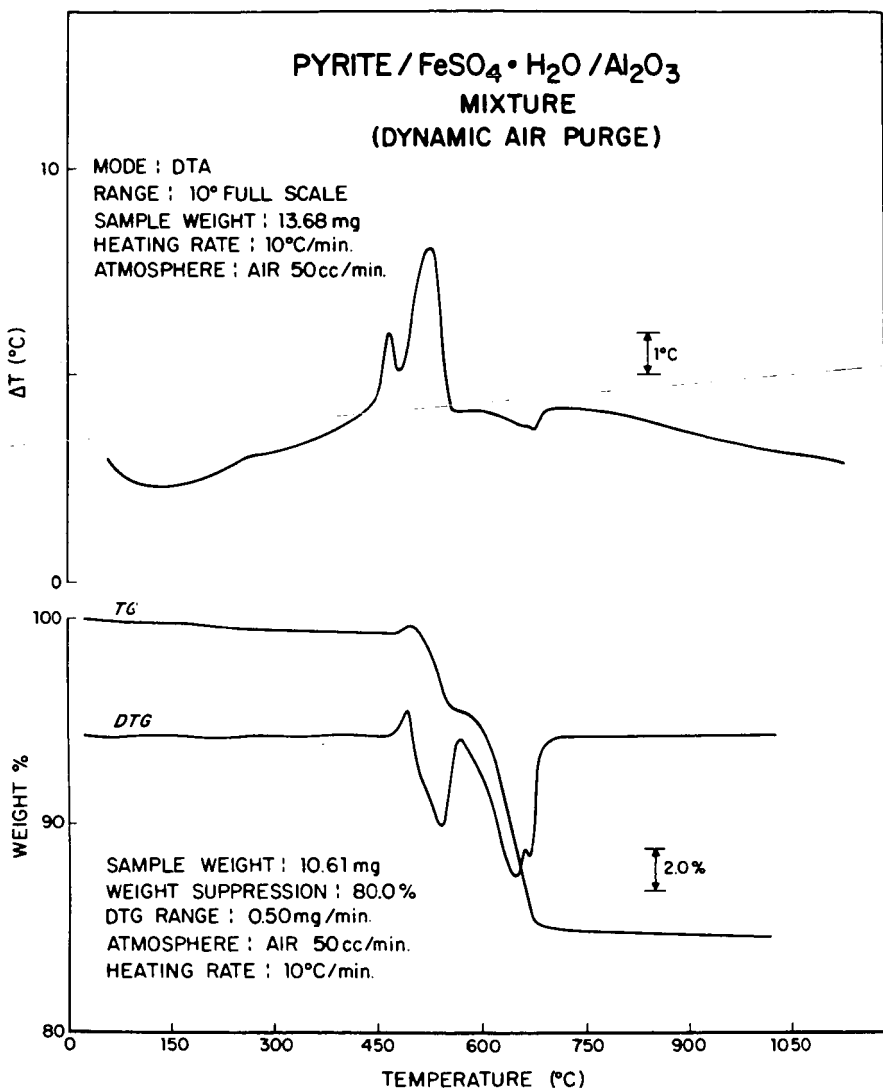


Figure 4.

DTA, TG, and DTG Thermal Curves for Pyrite/
 $\text{FeSO}_4 \cdot \text{H}_2\text{O} / \text{Al}_2\text{O}_3$ Synthetic Mixture

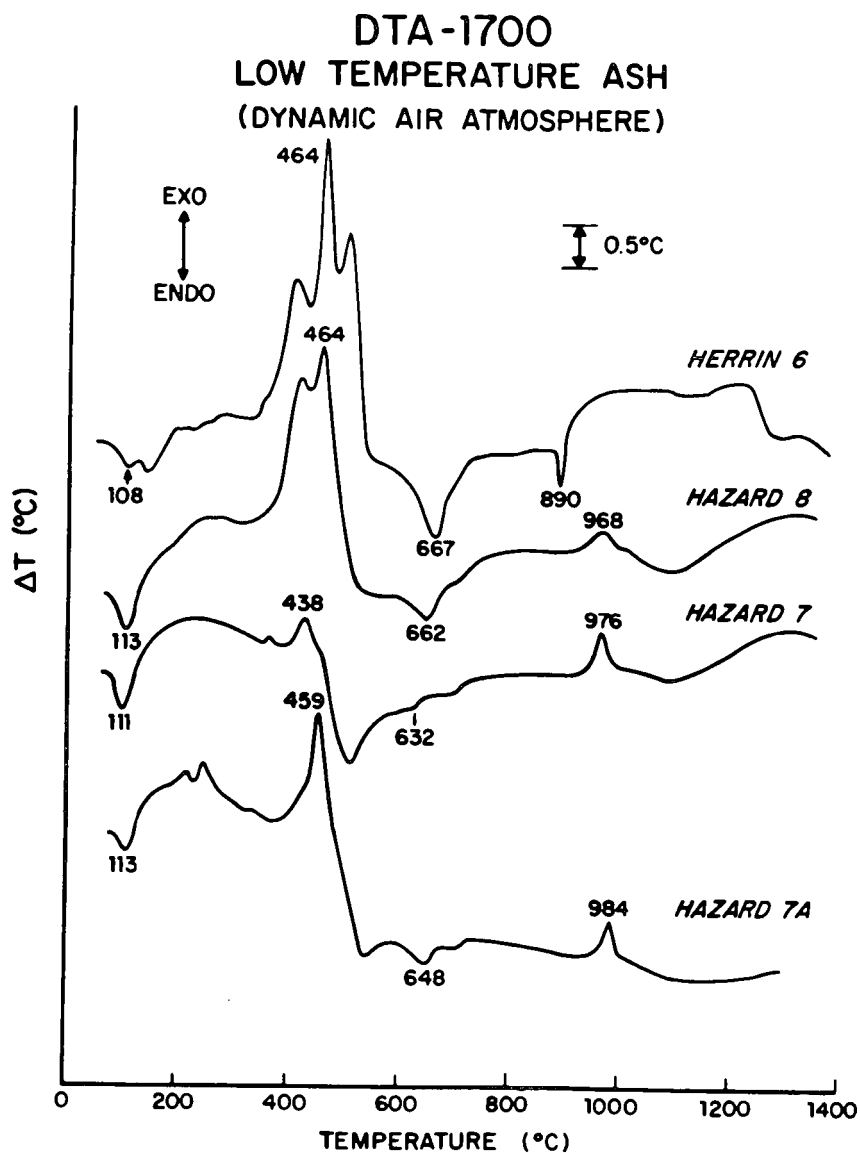


Figure 5